



In situ characterization of Pd₂Ga catalysts for methanol synthesis by Electron Microscopy and X-ray Diffraction

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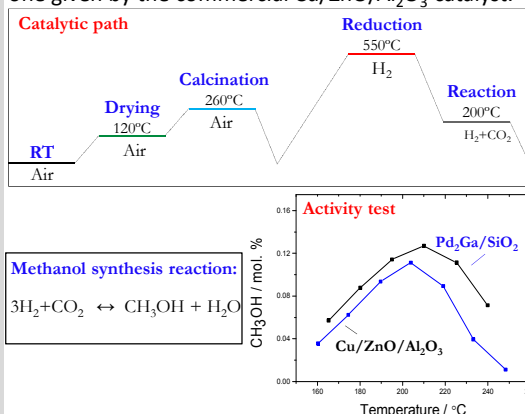
Introduction

Methanol (CH₃OH) is a chemical produced in 40 million tons per year[1] and amongst many applications, it can be used as a fuel or energy carrier. The synthesis is generally carried out from H₂ and CO at pressures up to 100 bar using a Cu/ZnO/Al₂O₃ catalyst. New materials able to synthesize methanol from H₂ and CO₂ at low pressure, such as Ni-Ga and Pd-Ga intermetallic compounds, have been predicted by DFT calculations and tested in a reactor [2,3]. In this study Pd₂Ga nanoparticles are investigated by complementary techniques such as XRD, TEM and ETEM, providing information on catalytic properties, size, morphology and crystal phase as summarized in the table.

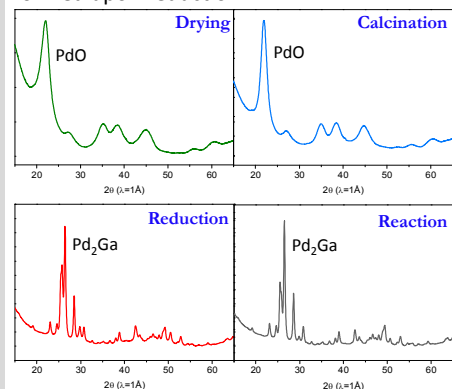
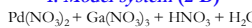
	Reactor	XRD	TEM	ETEM
Size distribution	No	(Yes)	Yes	Yes
Morphology	No	No	Yes	Yes
Crystal phase	No	Yes	Yes	Yes
Selectivity	Yes	(Yes)	No	No
Activity	Yes	(Yes)	No	No
Pressure	1 - 10 bar	10 ⁻⁶ - 1 bar	HV	5 mbar
Flow	5 Nl/min	100 Nml/min	-	10 Nml/min

Catalytic path and test of Pd₂Ga/SiO₂ (1 bar)

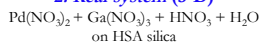
A high surface area (HSA) silica is impregnated with a solution of Pd and Ga nitrates in nitric acid. The catalyst is dried and calcined in air then reduced at 550°C in H₂. Methanol synthesis from H₂ and CO₂ is carried out in the range 160-250°C and the products are measured by gas chromatography. The yield from Pd₂Ga/SiO₂ catalyst is found to be higher than the one given by the commercial Cu/ZnO/Al₂O₃ catalyst.

**Investigation by *In-situ* XRD (1 bar)**

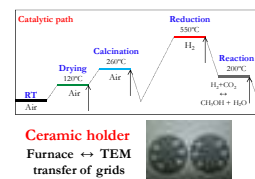
XRD patterns using synchrotron radiation are acquired at the 711 beam line of the *Max II Laboratory* (Lund, Sweden) during each step of the catalytic path to study the crystal phase and the alloy formation. During drying and calcination a PdO phase is observed (Ga₂O₃ is amorphous) and the active phase for the methanol synthesis is formed upon reduction.

**Sample preparation for TEM****1. Model system (2-D)**

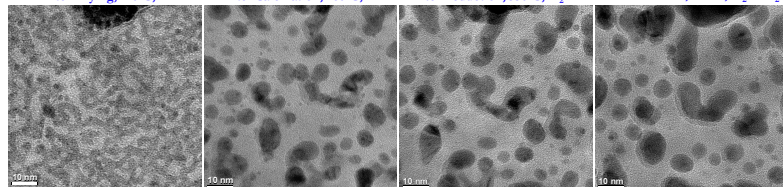
Impregnation on SiMPore grid

2. Real system (3-D)Deposition on Au/SiO₂ grid**TEM of identical location (HV)**

The catalytic path is carried out at 1 bar in a furnace (Anton Paar XRK 900) connected to a gas system and containing a ceramic holder for 6 TEM grids. After each step of the path (see arrows in the figure) the grids are transferred to the TEM (HV), where images of identical locations are acquired in order to follow the evolution of the catalysts through the path.

**1. TEM of identical location the *model catalyst***

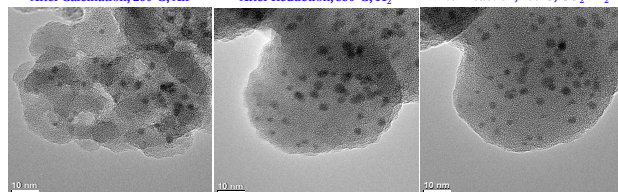
After Drying, 120°C, Air After Calcination, 260°C, Air After Reduction, 550°C, H₂ After Reaction, 200°C, H₂+CO₂



Images acquired at 200 kV, 285000 Magnification, Fei Technai

2. TEM of identical location for the *real catalyst*

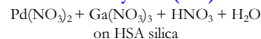
After Calcination, 260°C, Air After Reduction, 550°C, H₂ After Reaction, 200°C, CO₂+H₂



Images acquired at 200 kV, 285000 Magnification, Fei Technai

Between drying and calcination XRD shows that there is no changes in the crystal phase, whereas TEM images reveal a significant morphological change of the catalyst. During calcination the nanoparticle formation takes place and the size distribution is determined.

The supported nanoparticles are very stable through the catalytic path, although sintering of the support is observed. The particle size is smaller than for the model catalyst because of the interaction with the HSA silica support.

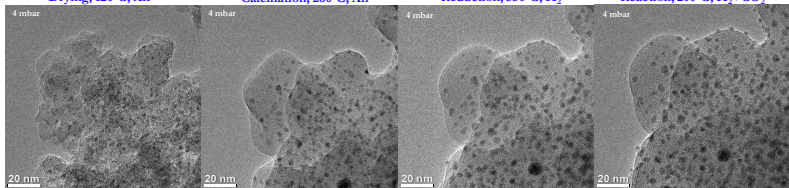
Sample preparation for ETEM**1. Real system (3-D)**

Deposition on Protochips

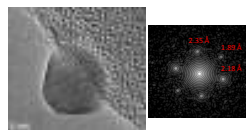
**ETEM (4 mbar)**

The test of the Pd₂Ga/SiO₂ nanoparticles in the reactor and the *In situ* XRD measurements are carried out at 1 bar, whereas the TEM images are acquired in vacuum. Repeating the whole catalytic path at 4 mbar in the ETEM enables to bridge the pressure gap between XRD and TEM and allows monitoring the catalyst evolution *in situ* and in real time.

Drying, 120°C, Air Calcination, 260°C, Air Reduction, 550°C, H₂ Reaction, 200°C, H₂+CO₂



Images acquired at 300 kV, 185000 Magnification, Fei Environmental Titan

Particle analysisHRTEM image show view along the [0 1 3] zone axis of Pd₂Ga**Conclusions**

- Pd₂Ga intermetallic compounds have been investigated by complementary techniques (Reactor measurement, XRD, TEM and ETEM).
- The test of the catalyst in the reactor shows that the methanol yield from Pd₂Ga/SiO₂ is higher to the one given by Cu/ZnO/Al₂O₃.
- XRD shows that the Pd₂Ga phase is formed upon reduction.
- Morphological changes and nanoparticle formation are observed by TEM imaging of identical locations and by ETEM experiments.
- Further investigation is required in order to further optimize the Pd₂Ga alloys for the methanol synthesis reaction from CO₂.